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MEASUREMENTS OF ALUMINUM OXIDE
KINETICS

William Felder, et al

AeroChem Research Laboratories, Incorporated

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The AeroChem high-temperature fast-flow reactor has been adapted to allow direct observation of AlO, $v = 0$ and 1 by laser-induced fluorescence. The rate coefficient k_1 for the homogeneous gas phase reaction $AlO + O_2 \rightarrow AlO_2 + O$ has been measured by this technique to be $(3.0 \pm 1.4) \times 10^{-13}$ ml molecule $^{-1}$ sec $^{-1}$ at 1370 ± 25 K. There is no discernible difference in k_1 for the AlO $v = 0$ and 1 levels. Using the collision frequency rate factor as an upper limit for k_1 , the measurements suggest an activation energy for this reaction of ≤ 0.8 eV, from		

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which it follows that $D(A_{10}-0) \geq 4.3$ eV.

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MEASUREMENTS OF ALUMINUM OXIDE KINETICS

Dr. William Felder
Dr. Arthur Fontijn

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SUMMARY

For several problems related to disturbed atmospheres, the identity and atmospheric lifetimes of metal oxides (particularly those of Al) need to be established. Using the AeroChem high-temperature fast-flow reactor¹ we have previously determined, by observing metal atom disappearance, the rate coefficients for the formation of $\text{AlO}^{2,3}$ and FeO^4 via the reactions of the free metal atoms with O_2 . The present work provides kinetic (and thermochemical) information on Al-oxide reactions. We report here the measurement of the rate coefficient of



at (1370 ± 25) K for AlO in the $v = 0$ and 1 (electronic ground state) vibrational levels, and a lower limit for the bond energy of AlO-O .

To measure k_1 we have modified the reactor to allow direct observation of AlO by laser-induced resonance fluorescence. To produce AlO, Al is vaporized, entrained in Ar, and O_2 added to this stream to form AlO via the rapid reaction



Reaction (1) is then studied by the addition of larger quantities of O_2 . Rate coefficients are obtained from the observed variations in the relative AlO concentration, $[\text{AlO}]_{\text{rel}}$, as a function of reaction time, $[\text{O}_2]$ and total pressure (or $[M]$). This basic technique developed for the present work is discussed in detail in the preceding semi-annual report on this contract.⁵ In this report we discuss further improvements in the apparatus optical measurement system which enabled measurements of k_1 for both $\text{AlO}(X^1\Sigma^+) v=0$ and 1 (Section II).

¹Fontijn, A., Kurzius S.C., Houghton, J.J., and Emerson, J.A., "Tubular Fast-Flow Reactor for High Temperature Gas Kinetic Studies," *Rev. Sci. Instr.* **43**, 726 (1972).

²Fontijn, A., Felder, W., and Houghton, J.J., "Tubular Fast-Flow Reactor Studies at High Temperatures. 2. Kinetics of the Al/O_2 Reaction," *AeroChem TP-304, Chem. Phys. Lett.*, in press; *Ibid.*, "Homogeneous and Heterogeneous Kinetics of the Atomic Al/O_2 Reaction in the 1000-1700 K Range," *AeroChem TP-306a, Fifteenth Symposium (International) on Combustion*, in press.

³Fontijn, A., Felder, W., and Houghton, J.J., "Kinetics of Al Atom Oxidation," *AeroChem TP-299, DNA 3242F*, September 1973.

⁴Fontijn, A., Kurzius, S.C., and Houghton, J.J., "High-Temperature Fast-Flow Reactor Studies of Metal-Atom Oxidation Kinetics," *Fourteenth Symposium (International) on Combustion* (The Combustion Institute, Pittsburgh, 1973) p. 167.

⁵Fontijn, A., and Felder, W., "Aluminum Oxide Kinetics," *Semi-Annual Report, AeroChem TP-307, RADC-TR-74-158*, March 1974.

The measurements (discussed in Section III) were made at pressures from 12-48 Torr and average gas velocities of 19-90 m sec⁻¹ at an average temperature of 1370 K. Within the precision of the measurement, the values of k_1 obtained are independent of both pressure and flow velocity, indicative of the bimolecular Reaction (1). The measurements indicate a value of $k_1 = (3.0 \pm 1.4) \times 10^{-13}$ ml molecule⁻¹ sec⁻¹ with no discernible difference between the $v = 0$ and 1 levels (which could be due to rapid vibrational relaxation at the relatively high temperatures of the present study). Using the collision frequency rate factor as an upper limit for k_1 , the measurement of k_1 suggests an activation energy for (1) of ≤ 0.8 eV, from which it follows that $D(\text{AlO-O}) \geq 4.3$ eV, a value midway between the two previously suggested extremes^{6,7} for this bond energy.

For further quantitative understanding of disturbed atmospheres, it appears necessary to extend the present measurements to lower temperatures (discussed in Section IV). Such measurements would allow an accurate determination of the activation energy for (1) and hence a more reliable limit of $D(\text{AlO-O})$ and would allow a better assessment of the difference, if any, in reactivity between $\text{AlO } v = 0$ and 1. To make useful predictions of the abundance of AlO and AlO_2 in disturbed atmospheres it is recommended that a study of reactions of O atoms be included in future work.

⁶Linevsky, M.J. and Alyea, F., "Spectroscopy of Metal Oxides," RADC-TR 73-391, November 1973.

⁷Farber, M., Srivastava, R.D., and Uy, O.M., "Mass Spectrometric Determination of the Heat of Formation of the AlO_2 Molecule," J. Chem. Phys. 55, 4142 (1971).

PREFACE

It is a pleasure to acknowledge the contributions of Richard L. Revolinski in performing the experimental work on this program and James J. Houghton for assisting in the construction of the apparatus and advising on its operation.

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I. INTRODUCTION

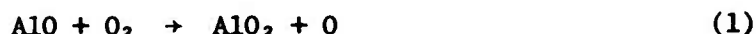
For several problems related to disturbed atmospheres, the identity and atmospheric lifetimes of metal oxides (particularly those of Al) need to be established. To obtain such knowledge one needs information not only on the reaction



which we have provided under the preceding Advanced Research Projects Agency/Defense Nuclear Agency contract,³ but also on further reactions in $\text{AlO}_x/\text{O}/\text{O}_2$ systems. The purpose of the present work is to provide kinetic, and hence also thermochemical, information on these reactions.

AlO is known to form following upper atmospheric releases of Al^0 and Al compounds.⁹ Additionally, the presence of AlO_2 may be anticipated. Since release experiments cannot provide the data needed to predict the time-space concentration history of these species and the processes in which they are involved, laboratory measurements are necessary. Prior to the present work, however, no laboratory kinetic information was available on the fate of AlO and AlO_2 in O/O_2 /inert gas atmospheres other than the measurements of the rate coefficient of Reaction (2) and its temperature dependence^{2,3} and the work of Linevsky⁶ on the global kinetics of the TMA/O-atom system.

In this report we describe the measurement of the absolute rate coefficient of



at 1370 K for AlO in the $v = 0$ and 1 vibrational levels. The implications of the measurements for the quantitative understanding of $\text{AlO}_x/\text{O}/\text{O}_2$ reaction systems are discussed.

⁸Golomb, D., "Results of AFCRL ALADDIN October 1973 Releases," Project IVY OWL Technical Progress Review Meeting, 12 February 1974.

⁹Rosenberg, N.W., Golomb, D., and Allen, E.F., Jr., "Resonance Radiation of AlO from Trimethyl Aluminum Released in the Upper Atmosphere," J. Geophys. Res. 69, 145 (1964).

II. EXPERIMENTAL

The kinetics of Reaction (1) were studied by directly observing AlO via laser-induced resonance fluorescence. The high-temperature fast-flow 'metal oxide' reactor and associated electro-optic systems used in these experiments have been described in detail previously.⁵ The HTV R212 detector photomultiplier tube (PMT) has been replaced with an EMI 9789 (bialkali) PMT, resulting in a more than tenfold increase in sensitivity due to an improvement in the signal-to-noise ratio, S/N.

As indicated in our previous report,⁵ the enhancement in S/N was necessary to allow measurements of AlO(X) $v = 0$ as well as $v = 1$. Such measurements were possible using the $0,0(B^2\Sigma^+-X^2\Sigma^+)$ bandhead fluorescence at 484.2 nm. It was necessary to employ a spectral bandwidth of ≈ 1.0 nm fwhm (0.25 mm slits) to resolve the 0,0 fluorescence from scattered 488.0 nm laser pumping radiation and 486.6 nm (1,1) fluorescence. Measurements pertaining to AlO $v = 1$ were obtained from fluorescence of the isolated (1,0) band at 464.8 nm, as previously described.⁵ These fluorescence transitions and others observed in our experiments are summarized in Fig. 1. The figure also indicates the accidental double pumping¹⁰ of both the 0,0 and 1,1 bands (from high ground state rotational levels) by the Ar⁺ 488.0 nm laser line.

The experimental procedures and data reduction method used in this work have been discussed at length.⁵ Although both stationary and traversing inlet mode data could be obtained, emphasis was placed on obtaining the more reliable^{2,3} traversing inlet data. In this mode, rate coefficients are obtained through the intermediate measurement of the pseudo-first order rate coefficient, $k_{ps_1} = -d \ln[AlO]_{rel}/dt$ (cf. Refs. 2, 3 and 5) illustrated in Fig. 2. The actual rate coefficients are obtained as the slopes of plots of k_{ps_1} vs $[O_2]$ (cf. Fig. 3 and Ref. 5).

¹⁰Johnson, S.E., Capelle, G., and Broida, H.P., "Laser Excited Fluorescence and Radiative Lifetimes of AlO($B^2\Sigma^+-X^2\Sigma^+$)," J. Chem. Phys. 56, 663 (1972).

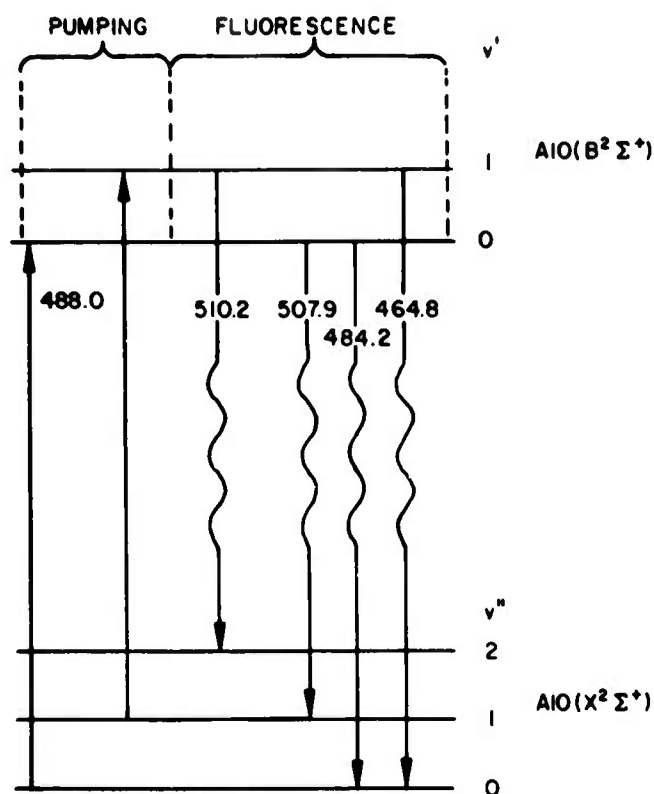


Figure 1. Summary diagram of $\text{AlO}(\text{B-X})$ system showing Ar^+ laser pumping and observed fluorescence transitions.

III. RESULTS AND DISCUSSION

The k_1 measurements are summarized in Table 1 for the $v = 0$ and $v = 1$ vibrational levels of AlO . Within the experimental uncertainty, there is no measurable difference between the observed k_1 values for these states. Also within the experimental uncertainty, the data show no dependence on total pressure or flow velocity between 12 and 48 Torr and 19 and 90 m sec^{-1} indicative of the two-body process, Reaction (1).

The mean rate coefficients, $k_1^{(0)}$ and $k_1^{(1)}$, obtained from the data are 2.9×10^{-13} and 3.0×10^{-13} $\text{ml molecule}^{-1} \text{sec}^{-1}$, respectively. The normalized standard deviations are 52% and 33%, respectively. Allowing for a possible 20% systematic error¹¹ and the 23% uncertainty in η^{11} the recommended values for k_1 at 1370 K are $k_1^{(0)} \approx k_1^{(1)} = (3.0 \pm 1.4) \times 10^{-13}$ $\text{ml molecule}^{-1} \text{sec}^{-1}$. To our knowledge, this is the first measurement of k_1 .

¹¹Ferguson, E.E., Fehsenfeld, F.C., and Schmeltekopf, A.L., "Flowing Afterglow Measurements of Ion-Neutral Reactions," *Advances in Atomic and Molecular Physics* 5, 1 (1969).

TABLE 1. SUMMARY OF MEASUREMENTS IN THE AlO/O_2 SYSTEM

P (Torr) ^a	$[M]$ (10^{16} ml ⁻¹)	$\lambda_{\text{fluor.}}$ (nm)	$[\text{O}_2]$ (10^{14} ml ⁻¹)	\bar{T} (K)	\bar{v} (m sec ⁻¹)	$k_1^{(o)b}$ (10^{-13} ml molecule ⁻¹ sec ⁻¹)	$k_1^{(i)b}$ (10^{-13} ml molecule ⁻¹ sec ⁻¹)
12	8.6	484.2	1.3 to 13	1350	19	2.5	
12	8.4	464.8	1.3 to 25	1330	19		2.6
12	8.3	464.8	0.13 to 24	1395	41		3.4
12	8.3	464.8	1.2 to 13	1387	41		3.7
12	8.5	484.2	0.5 to 8.2	1367	90	4.5	
12	8.4	464.8	0.1 to 22	1383	87		3.4 ^c
24	17.3	464.8	0.3 to 13	1330	19		1.8
24	17.0	484.2	0.3 to 20	1368	88	1.8	
24	16.8	464.8	2.5 to 21	1380	78		2.3
48	34.0	464.8	1.2 to 21	1363	40		4.8
Avg. d						2.9 ± 1.5	3.0 ± 1.0

^a 1 Torr = 133.3 Pa.

^b Superscript indicates vibrational level of AlO.

^c Stationary inlet at 20 cm from observation port.

^d Mean value and standard deviation.

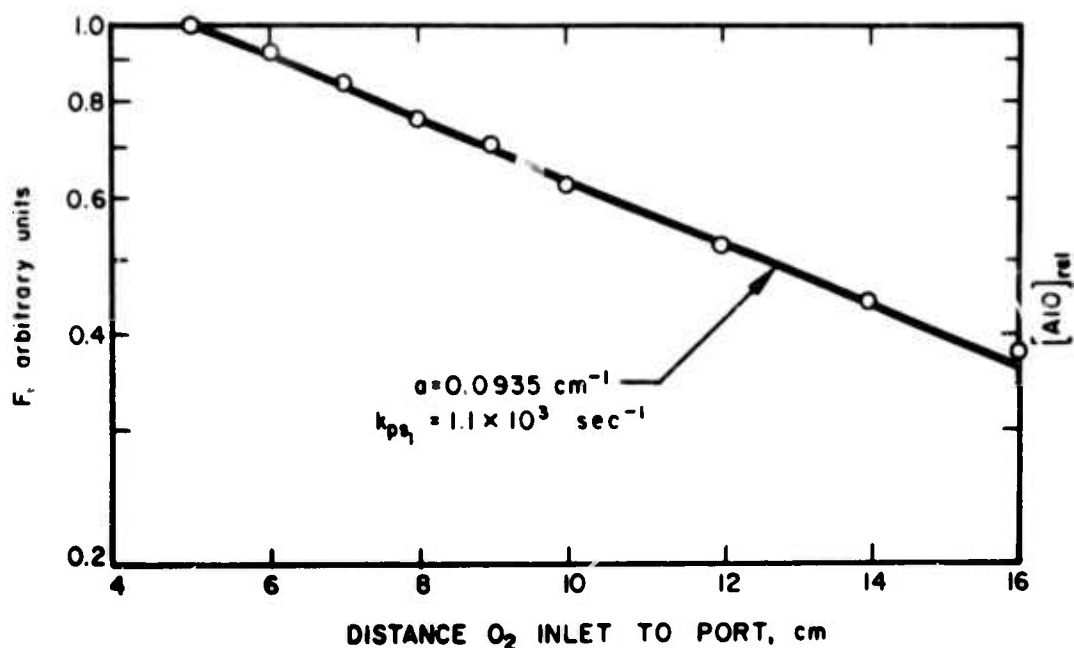


Figure 2. A10 ($v = 1$) concentration profile. $\bar{T} = 1370$ K;
 $\bar{v} = 90$ m sec; $[O_2] = 5.4 \times 10^{14}$ ml⁻¹; $\lambda_{\text{fluor}} = 464.8$ nm;
 $P = 24$ Torr ($[M] = 16.9 \times 10^{16}$ ml⁻¹).

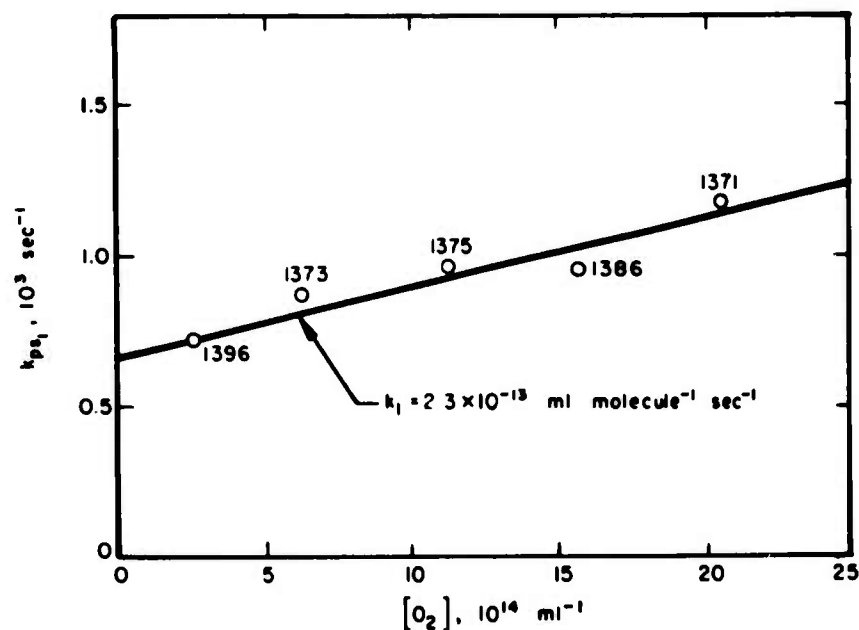


Figure 3. A10 ($v = 1$)/O₂ rate coefficient from k_{ps_1} measurement.
 $\bar{T} = 1380$ K; $v = 78$ m sec⁻¹; $\lambda_{\text{fluor}} = 464.8$ nm; $P = 24$ Torr
 $([M] = 16.8 \times 10^{16}$ ml⁻¹). Numbers by each point indicate the
 temperature at which it was obtained.

The thermochemistry of Reaction (1) is not well known. Farber et al.⁷ determined a value of ~ 0 eV for the heat of reaction based on Knudsen cell effusion-mass spectrometer measurements. Linevsky⁶ has suggested that the reaction could be as much as 1.7 eV endothermic based on the onset of the 'AlO₂ continuum' observed in his studies of the O atom/TMA system. Since the pre-exponential of k_1 cannot exceed the collision frequency rate factor ($\sim 3 \times 10^{10}$ ml molecule⁻¹ sec⁻¹) the above value of k_1 indicates an activation energy of ≤ 0.8 eV for Reaction (1), and hence an upper limit of 0.8 eV for the reaction endothermicity.

The present observations show that the rates of disappearance of AlO $v = 0$ and 1 are equal under identical reaction conditions. This is a necessary, but not sufficient, result to show that $k_1^{(0)} = k_1^{(1)}$. In the absence of rapid vibrational equilibration, the interpretation that $k_1^{(0)} = k_1^{(1)}$ is correct. If vibrational equilibration is rapid, the measurement is indicative of the most rapid rate coefficient of the two, presumably $k_1^{(1)}$. Although the vibrational equilibration cannot be assessed quantitatively since the vibrational relaxation of AlO $v = 1 \rightarrow 0$ ($\omega_e \sim 978$ cm⁻¹) has not been studied in either direction, it is known that molecules such as O₂ ($\omega_e \sim 1550$ cm⁻¹) and Cl₂ ($\omega_e \sim 550$ cm⁻¹) are relaxed by Ar at 1400 K ($v = 1 \rightarrow 0$) in about 1×10^4 and 1×10^3 gas kinetic collisions, respectively.¹² The number of collisions necessary for vibrational excitation ($v = 0 \rightarrow 1$) is related to the number required for relaxation by

$$Z_{0 \rightarrow 1}/Z_{1 \rightarrow 0} = e^{\Delta E/kT} \quad (3)$$

where $Z_{0 \rightarrow 1}$ and $Z_{1 \rightarrow 0}$ are the number of collisions required for excitation and relaxation respectively, and ΔE is the 0-1 vibrational energy spacing. At 1400 K, kT equals 973 cm⁻¹ (0.12 eV) and the excitation thus would require between $\sim 5 \times 10^4$ and $\sim 2 \times 10^3$ gas kinetic collisions for O₂ and Cl₂, respectively. $k_1^{(0)}$ and $k_1^{(1)}$ would not be distinguishable if vibrational equilibration is rapid compared to the time resolution of our experiments, which, at the highest flow velocities used, is $\sim 10^{-6}$ sec.

¹²Stevens, B., Collisional Activation in Gases, Volume 3 International Encyclopedia of Physical Chemistry and Chemical Physics, ed. A.F. Trotman-Dickenson (Pergamon Press, New York, 1967) p. 201.

During this time an AlO molecule suffers about 10^3 collisions with Ar at 10 Torr. Thus $k_1^{(0)}$ and $k_1^{(1)}$ measurements may be equivalent under the reaction conditions used.

Extension of the measurements to lower temperatures and pressures appears to be much needed to determine the activation energy and a lower limit for D(AlO-O). The combination of these experiments with knowledge of the activation energy gained from the temperature dependence of k_1 would allow a better assessment of the possible role of vibrational excitation. The results of work by the groups of Braun^{13,14} and Polanyi^{15,16} suggest that differences in the rate coefficients due to vibrational excitation in the reactants can be directly observed at room temperature in reactions having appreciable activation energies.

In our previous report⁵ it was shown that a value for k_2 would in principle be obtained by measuring the initial rate of AlO appearance subject to the condition that $k_2[O_2]t \ll 1$. Calculations indicate that the values of $[O_2]$ required to achieve this condition within the range of conveniently accessible flow conditions are of the same magnitude as the initial $[Al]$ ($\approx 10^{11}$ - 10^{12} ml⁻¹) used. Under the conditions of the present experiments this would violate the pseudo-first order kinetics criterion on which the measurement is based. From the present work, it is, however, possible to conclude⁵ that $k_2 \geq 100 k_1$, in agreement with the measurements of $k_1 = 3 \times 10^{-13}$ ml molecule⁻¹ sec⁻¹ and our previous^{2,3} measurement of $k_2 = 3 \times 10^{-11}$ ml molecule⁻¹ sec⁻¹. The accurate measurement of k_2 using AlO appearance may be possible by drastically reducing initial $[Al]$. Such a reduction would necessarily require a compensating increase in the sensitivity of the $[AlO]_{rel}$ optical measurement system. Since an accurate value of k_2 has been provided in our previous work^{2,3} and since the measurement of k_2 was not a goal of the present work, these experiments were not pursued.

¹³Kurylo, M.J., Braun, W., Kaldor, A., Freund, J.M., and Wayne, R.P., "Infrared Laser Enhanced Reactions: Chemistry of Vibrationally Excited O_3 with NO and $O_2(^1\Delta)$," J. Photochem., in press.

¹⁴Kaldor, A., Braun, W., and Kurylo, M.J., "Infrared Laser Enhanced Reactions: $O_3 + SO$," to be submitted for publication.

¹⁵Douglas, D.J., Polanyi, J.C., and Sloan, J.J., "Effect of Reagent Vibrational Excitation on the Rate of a Substantially Endothermic Reaction: $HCl(v' = 1-4) + Br \rightarrow Cl + HBr$," J. Chem. Phys. **59**, 6679 (1973).

¹⁶Polanyi, J.C., "Some Concepts in Reaction Dynamics," Acc. Chem. Res. **5**, 161 (1972).

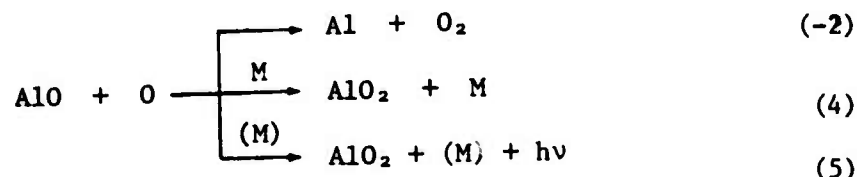
IV. CONCLUSIONS AND RECOMMENDATIONS

This work has established the feasibility of studying reactions involving AlO as reactant. The rate coefficient for the reaction



has been measured to be $(3.0 \pm 1.4) \times 10^{-13}$ ml molecule⁻¹ sec⁻¹ at 1370 K. The magnitude of this rate coefficient indicates that the reaction cannot be more than 0.8 eV endothermic and hence that $D(\text{AlO-O}) \geq 4.3$ eV. To assess the role of AlO and AlO₂ in disturbed atmospheres it is necessary to establish the temperature dependence of k_1 . In particular, knowledge of the value of k_1 at lower temperatures appears to be needed. Measurements at lower temperatures, which can readily be made by the technique used in this work, would allow the determination of the activation energy of the reaction and would yield a more accurate lower limit for $D(\text{AlO-O})$. Such measurements would also allow a better assessment of the difference, if any, in reactivity between AlO ($v = 0$ and 1), which is inherent to the phenomenology of disturbed atmospheres.

To make accurate predictions on the abundance of AlO and AlO₂ in disturbed atmospheres it is necessary to consider not only reactions of O₂ but also of O. Such measurements, which can be undertaken in the flow reactor used in the present work should include kinetic measurements on the competing reactions



As discussed in the preceding report on this contract,⁵ the value of the equilibrium constant $K_2(T)$ is not known with sufficient accuracy to predict k_{-2} from k_2 at the temperatures of interest. No kinetic information on Reaction (4) is available. There now exists considerable doubt¹⁷ whether Reaction (6) is responsible for the apparent continuum emission observed in upper atmospheric Al releases. This makes a direct study of emission from AlO/O, and/or its suggested alternatives,¹⁷ all the more interesting. Linevsky⁶ places the onset of the continuum at ≈ 340 nm. Our measurement of $D(\text{AlO-O}) \geq 4.3$ eV would allow an onset of ≈ 290 nm. If further work shows $D(\text{AlO-O})$ to be considerably larger, doubt as to the importance of (5) as the excitation reaction would be increased. Thus the measurement of $D(\text{AlO-O})$ via the determination of the activation

¹⁷ Kolb, C.E., Herschbach, D.R., and Gersh, M.E., "An Analysis of the Visible Chemiluminescence Observed in the Gas-Phase Oxidation of Aluminum and Its Compounds," RADC-TR-74-163, April 1974.

energy of Reaction (1) and the elucidation of the continuum emission excitation are related problems, the solutions to either one of which would be helpful in interpreting the other.

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